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54 **Multi-stage polymers having alkali-soluble and alkali-insoluble stages.**

57 Water-resistant multi-stage polymers having an alkali-insoluble polymer and an alkali-soluble polymer are prepared by sequential emulsion polymerization of a monomer mixture having acid functionality in the alkali-soluble stage and, optionally, a polyfunctional compound, the alkali-insoluble polymer having, optionally, an amine functionality, such that the resulting polymer has an alkali-insoluble polymer stage and an alkali-soluble polymer stage. Films prepared using the multi-stage composition and method of this invention are particularly useful in semi-transparent wood stain binders.

This invention relates to water-resistant multi-stage polymers and a process for preparing the same. This invention also relates to improved multi-stage polymers having an alkali-insoluble emulsion polymer and an alkali-soluble emulsion polymer. This invention further relates to a sequential emulsion polymerization process wherein the alkali-soluble polymer and the alkali-insoluble polymer are substantially physically or chemically associated.

Mixtures and blends of soluble resins with insoluble emulsion polymers are known and are generally used as binders in ink formulations, and as overprint coatings to protect the printed substrate. The soluble resins were generally prepared by solution polymerization, such as described in US-A-3,037,952. Core-shell resins made significant improvements over mixtures and blends of the prior art, such as those described in US-A-4,916,171. By polymerizing one component in the presence of the other to form core-shell compositions, such as described in '171, improvements in production efficiency, in stability, and in rheology were realized. Improvements in core-shell compositions were again realized by chemically-grafted core-shell polymers.

By using a polyfunctional compound to graft chemically the core to the shell, as described in US-A-4,876,313, core-shell compositions were useful in areas where formulation-stability was required. What is required is a durable multi-stage polymer composition. These multi-stage compositions must be resistant to water such that when used as a coating in an outside environment, the coated substrate is protected.

US-A-5,073,591 discloses a method for producing an acidic, concentrated, polymeric emulsion that can be diluted and thereafter neutralized to provide a novel thickener. The patent discloses a two-stage method wherein the first stage contains a high level of acid monomer and a crosslinker, and the second stage contains an amino-containing monomer.

Japanese Patent Application J 01-185311A discloses a method for producing polymer particles having internal voids which are useful as light diffuser or light diffuser aids for paper, fiber and leather coatings. The alkali-swellable particle of this invention is made by emulsion polymerization of a monomer containing a carboxylic acid monomer and at least one unsaturated carboxylic acid monomer.

US-A-4,923,919 discloses a process for producing an acrylic emulsion polymer as the polymer component of a pressure-sensitive adhesive. This acrylic emulsion is made in the presence of an alkali-dissolved or alkali-dispersed polymer resin. The acrylic emulsion polymer, polymerized in the presence of the polymer support resin, usually contains monomers to increase the molecular weight and internal strength of the polymer backbone. The acrylic emulsion of this invention is particularly useful as an adhesive.

US-A-4,916,171 discloses a process for making polymers comprising alkali-insoluble core and an alkali-soluble shell and compositions thereof. Core shell polymers made according to the process of this invention are stated to be suitable for use in coatings, pigmented paints, clear overprint varnishes, aqueous flexographic inks, polymer coatings for leather and floor polishes and cement compositions.

US-A-4,876,313 discloses a process for making alkali-insoluble core and an alkali-soluble shell polymer utilizing compounds which chemically graft the core and the shell together. The core shell polymers of this invention are particularly useful in inks, coatings, varnishes, floor polishes, leather treatment and cement formulations.

The present invention seeks to overcome the problems associated with the prior art polymers and compositions.

According to a first aspect of the present invention there is provided a water-resistant composition comprising a multi-stage polymer prepared by a sequential emulsion polymerization process comprising an alkali-soluble stage and an alkali-insoluble stage wherein the alkali-soluble stage has an acid functionality greater than the acid functionality of the alkali-insoluble stage and wherein the alkali-insoluble stage is prepared in the presence of the alkali-soluble stage.

According to a second aspect of the present invention there is provided a semi-transparent wood stain binder comprising the multi-stage alkali-soluble polymer and alkali-insoluble composition of the first aspect of the present invention.

According to a third aspect of the present invention there is provided a method for producing a water-resistant multi-stage polymer prepared by a sequential emulsion polymerization process comprising forming in a first stage a mixture of monomers comprising from about 40 percent to about 90 percent of an alkyl acrylate or methacrylate and from about 10 percent to 60 percent of a carboxylic acid, polymerizing the mixture to form the alkali-soluble polymer, forming in a second stage a mixture of monomers comprising from about 65 percent to about 100 percent of an alkyl acrylate or methacrylate and from about 0 percent to 10 percent of a carboxylic acid, adding the second-stage monomers mixture to the polymerized first stage monomers, and polymerizing the second stage monomers to form an insoluble polymer and wherein the alkali-soluble polymer is neutralized with a base and substantially dissolved to form a blend of neutralized alkali-soluble and alkali-insoluble polymer and an aqueous solution of neutralized alkali-soluble polymer.

According to a fourth aspect of the present invention there is provided a method for producing a water-

resistant multi-stage polymer comprising forming in a first stage a mixture of monomers comprising from about 40 percent to about 90 percent of an alkyl acrylate or methacrylate and from about 10 percent to 60 percent of a carboxylic acid, polymerizing the mixture to form the alkali-soluble polymer, neutralizing and solubilizing the alkali-soluble polymer with an amine or base, forming in a second stage a mixture of monomers comprising from about 65 percent to about 100 percent of an alkyl acrylate or methacrylate and from about 0 percent to 10 percent of a carboxylic acid, and polymerizing the second stage monomers to form an alkali-insoluble polymer.

According to a fifth aspect of the present invention there is provided a method for producing a water-resistant multi-stage polymer prepared by a sequential emulsion polymerization process comprising forming in a first stage a mixture of monomers comprising from about 40 percent to about 90 percent of an alkyl acrylate or methacrylate and from about 10 percent to 60 percent of a carboxylic acid polymerizing the mixture to form the alkali-soluble polymer, forming in a second stage a mixture of monomers comprising from about 65 percent to about 100 percent of an alkyl acrylate or methacrylate and from about 0 percent to 10 percent of a carboxylic acid and from about 0 percent to 15 percent, preferably from about 0 percent to about 10 percent of a monomer having amine functionality, adding the second-stage monomers mixture to the polymerized first stage monomers, and polymerizing the second stage monomers to form an insoluble polymer and wherein the alkali-soluble polymer is neutralized with a base and substantially dissolved to form a blend of neutralized alkali-soluble and alkali-insoluble polymer and an aqueous solution of neutralized alkali-soluble polymer.

According to a sixth aspect of the present invention there is provided a semi-transparent wood stain binder comprising the multi-stage composition having an alkali-soluble polymer stage and an alkali-insoluble polymer stage prepared according to any one of the method aspects of the present invention.

The multi-stage polymers of the invention are particularly useful as semi-transparent stains. Other advantages are that the multi-stage polymers are capable of being used in environments where water-resistance is an essential factor and that they exhibit enhanced durability.

Preferably the alkali-soluble polymer is polymerized from a mixture of monomers comprising from about 40 percent to about 90 percent of an alkyl acrylate or methacrylate and the alkali-insoluble polymer is polymerized from a mixture of monomers comprising from about 65 percent to about 100 percent of an alkyl acrylate or methacrylate, preferably wherein the alkyl acrylate and methacrylate monomers for the alkali-soluble and alkali-insoluble polymers are selected from the group consisting of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, hydroxy ethyl acrylate, hydroxyethyl methacrylate, butyl methacrylate, acrylonitrile, styrene, substituted styrene, vinyl acetate, vinyl chloride, and other C₁ to C₁₂ alkyl acrylates and methacrylates.

Preferably the alkali-soluble polymer is polymerized from a mixture of monomers having acid functionality comprising from about 10 percent to about 60 percent, preferably from about 15 percent to about 55 percent based on the weight of the alkali-soluble polymer stage selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, acrylic anhydride, methacrylic anhydride, itaconic anhydride, and fumaric anhydride.

Preferably the alkali-insoluble polymer is polymerized from a mixture of monomers having acid functionality comprising from up to about 10 percent, based on the weight of the alkali-insoluble polymer stage.

Preferably the alkali-insoluble polymer is polymerized from a mixture of monomers having acid functionality comprising from about 0.5 percent to about 5 percent, based on the weight of the alkali-insoluble polymer stage.

Preferably the alkali-soluble polymer is neutralized with a base and substantially dissolved to form a blend of neutralized alkali-soluble and alkali-insoluble polymer and an aqueous solution of neutralized alkali-soluble polymer.

Preferably the base is selected from the group consisting of ammonia, triethyl amine, monoethanolamine, dimethylaminoethanol, aminomethylpropanol, sodium hydroxide and potassium hydroxide.

Preferably the weight ratio of alkali-insoluble polymer to the alkali-soluble polymer is from about 85:15 to about 15:85.

Preferably the weight ratio of alkali-insoluble polymer to the alkali-soluble polymer is from about 70:30 to about 30:70.

Preferably the weight ratio of alkali-insoluble polymer to the alkali-soluble polymer is from about 60:40 to about 40:60.

Preferably the alkali-soluble polymer having a weight average molecular weight of about 5,000 to about 50,000 and the alkali-insoluble polymer having a weight average molecular weight of greater than 50,000, as determined by gel permeation chromatography.

Preferably the glass transition temperature (T_g) of the alkali-insoluble polymer is from about minus (-) 65 degrees centigrade to about 100 degrees centigrade.

Preferably the glass transition temperature (T_g) of the alkali-insoluble polymer is from about minus (-) 65

degrees to about 30 degrees centigrade.

Preferably the glass transition temperature (T_g) of the alkali-soluble polymer is from about minus (-) 20 to about 100 degrees centigrade.

5 Preferably the glass transition temperature (T_g) of the alkali-soluble polymer is from about minus (-) 20 to about 75 degrees centigrade.

Preferably the alkali-insoluble stage has amine functionality.

10 Preferably the alkali-insoluble polymer is polymerized from a mixture of monomers having amine functionality comprising from about 0 percent to about 15 percent, preferably from about 0 percent to about 10 percent based on the weight of the alkali-insoluble polymer and wherein the amine functional monomer is selected from the group consisting of tert-butylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylamide, dimethylaminoethyl (meth)acrylate, oxazolidinylethyl (meth)acrylate, vinylbenzylamines, vinylphenylamines, 2-vinylpyridines or 4-vinylpyridines, p-aminostyrenes, substituted diallyl-amines, vinylpiperidines, vinylimidizoles, 2-morpholinoethyl (meth)acrylate, acrylamide, methacrylamide, N-substituted (meth)acrylamides, methacrylamidopropyl trimethyl ammonium chloride (MAPTAC), diallyl dimethyl ammonium chloride (DADMAC), 2-trimethyl ammonium ethyl methacrylic chloride (TMAEMC), quaternary amine salts of substituted (meth)acrylic and (meth)acrylamido monomers.

Preferably the alkali-soluble polymer and the alkali-insoluble polymer are chemically grafted together using one or more polyfunctional compounds having two or more sites of unsaturation of unequal reactivity.

20 Preferably the polyfunctional compounds are selected from the group consisting of dicyclopentenylxyethyl-, dicyclopentenyl-, allyl-, methallyl-, vinyl- and crotyl-esters of acrylic, methacrylic, maleic (mono- and di-esters), fumaric (mono- and di-esters) and itaconic (mono- and di-esters) acids; allyl-, methallyl- and crotyl-vinyl ether and thioether; N- and N,N-di-allyl-, methallyl-, crotyl- and vinyl-amides of acrylic and methacrylic acids; N-allyl-, methallyl- and crotyl-maleimide; vinyl esters of 3-butenic and 4-pentenoic acids; diallyl phthalate; triallyl cyanurate; O-allyl-, methallyl-, crotyl-, O-alkyl-, aryl-, P-vinyl-, P-allyl-, P-crotyl- and P-methallyl-phosphonates; triallyl-, trimethallyl- and tricrotyl-phosphates; O-vinyl-, O,O-diallyl-, dimethallyl- and dicrotyl-phosphates; cycloalkenyl esters of acrylic, methacrylic, maleic (mono- and di-esters), fumaric (mono- and di-esters) and itaconic (mono- and di-esters) acids; vinyl ethers and vinyl thioethers of cycloalkenols and cycloalkene thiols; vinyl esters of cycloalkene carboxylic acids; 1,3-butadiene, isoprene and other conjugated dienes; paramethylstyrene; chloromethylstyrene; allyl-, methallyl-, vinyl- and crotyl-mercaptan; cycloalkenyl-, allyl-, methallyl-, vinyl- and crotyl-mercaptopropionates; cycloalkenyl-, allyl-, methallyl-, vinyl- and crotyl-mercaptoacetates; bromotrichloromethane; bromoform; carbon tetrachloride; and carbon tetrabromide.

Preferably the polyfunctional compound is present in the alkali-soluble polymer or alkali-insoluble polymer at a level of from about 0 percent to about 10 percent based on the weight of the polymer.

35 Preferably the polyfunctional compound is present in the alkali-soluble polymer or alkali-insoluble polymer at a level of from about 0 percent to about 7 percent, based on the weight of the polymer.

Preferably the method includes chemically grafting together the alkali-soluble polymer and the alkali-insoluble polymer using one or more polyfunctional compounds having two or more sites of unsaturation of unequal reactivity, preferably using a compound as defined above.

40 This invention therefore relates to a water-resistant composition having a multi-stage polymer with an alkali-soluble stage and an alkali-insoluble stage where the acid functionality of the alkali-soluble stage is greater than the acid functionality of alkali-insoluble stage where the alkali-soluble and alkali-insoluble stages are prepared by a sequential emulsion polymerization process and where the alkali-insoluble stage is prepared in the presence of the alkali-soluble stage.

45 Multi-stage polymers prepared according to the method of this invention are useful in environments where water-resistance and durability are important, while maintaining the lapping required in semi-transparent stain applications.

50 This invention relates to multi-stage polymers that are substantially physically or chemically associated and their use in applications where water-resistance and durability are required. The multi-stage polymers of this invention are such that upon dissolving the alkali-soluble stage with an alkali compound, the alkali-insoluble stage and a portion of the dissolved alkali-soluble stage continue to remain substantially physically or chemically associated together.

55 In another aspect of the present invention, the multi-stage polymers are substantially physically or chemically associated by polymerizing a monomer mixture containing at least one monomer having acid functionality to form an alkali-soluble polymer, and in a separate polymerization step and in the presence of the previously formed alkali-soluble polymer, polymerizing a mixture of monomers which may, optionally, contain at least one monomer having amine functionality to form an alkali-insoluble polymer.

The alkali-soluble polymers of this invention are prepared by using at least one monomer having acid functionality. Suitable monomers having such acid functionality include those selected from the group consisting

of acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, acrylic anhydride, methacrylic anhydride, itaconic anhydride, and fumaric anhydride and the like.

Suitable levels of monomers having acid functionality for use in the alkali-soluble polymer range from about 10 percent to about 60 percent by weight, preferably from about 15 percent to about 55 percent by weight of the alkali-soluble polymer. Higher acid levels are used in the alkali-soluble stage polymer than in the alkali-insoluble stage polymer to insure solubility. It is believed that the alkali-soluble polymer provides the redispersibility required for good lapping in semi-transparent stains. It is also further believed that the continued association of the soluble and insoluble polymers after inducing solubility, by adding an amine or base, provide the multi-stage polymers of this invention with their water-resistance and durability.

Suitable non-acid functional monomers for preparing the alkali-soluble polymer include levels from about 40 percent to about 90 percent of alkyl acrylate or methacrylate selected from the group consisting of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, isodecyl methacrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, hydroxy ethyl acrylate, hydroxyethyl methacrylate, butyl methacrylate, acrylonitrile, styrene, substituted styrene, vinyl acetate, vinyl chloride, and other C₁ to C₁₂ alkyl acrylates and methacrylates, and the like.

The alkali-soluble polymer has a weight average molecular weight less than that of the alkali-insoluble polymer. The weight average molecular weight is from about 5,000 to about 50,000, as determined by gel permeation chromatography. The composition of the alkali-soluble polymer may contain any chain-transfer agent, or mixtures thereof, to control molecular weight. Suitable chain transfer agents include, for example, C₁ to C₁₂ alkyl or functional alkyl mercaptans or alkyl or functional alkyl mercaptoalkanoates or halogenated hydrocarbons and may be employed in the soluble polymer at levels of from about 0.1 percent to about 10 percent by weight of the alkali-soluble polymer.

The Tg of a polymer is a measure of the hardness and melt flow of the polymer. The higher the Tg, the less the melt flow and the harder the coating. Tg is described in *Principles of Polymer Chemistry* (1953), Cornell University Press. The Tg can be actually measured or it can be calculated as described by Fox in *Bull. Amer. Physics Soc.*, 1, 3, page 123 (1956). Tg, as used herein, refers to actually measured values. For measurement of the Tg of a polymer, differential scanning calorimetry (DSC) can be used (a rate of heating of 10°C 20 minute, with Tg taken at the first inflection point). The Tg of the alkali-soluble polymer of the invention is from about minus (-) 20 to about 100 degrees centigrade, and more preferably, from about minus (-) 20 to about 75 degrees centigrade.

The alkali-insoluble polymers are prepared from the same list of non-acid functional monomers used in the preparation of the alkali-soluble polymers. Suitable levels include from about 65 percent to about 100 percent of alkyl acrylate or methacrylate and the like.

Monomers having acid-functionality may also be copolymerized with the nonacid functional monomers in the preparation of alkali-insoluble polymer. However, the alkali-insoluble polymer must have less than 10% by weight of monomers having acid functionality, such that the alkali-insoluble polymer is insoluble in alkaline solutions. Suitable levels of acid containing monomers that could be included in the alkali-insoluble polymer range from about zero (0) percent to about 10 percent, preferably from about 0.5 percent to about 5 percent by weight, based on the weight the alkali-insoluble polymer.

The alkali-insoluble polymer has a weight average molecular weight greater than 50,000, as determined by gel permeation chromatography. The glass transition temperature (Tg) of the alkali-insoluble polymer of this invention is from about minus (-) 65 degrees centigrade to about 100 degrees centigrade, and preferably minus (-) 65 degrees to about 30 degrees centigrade.

The alkali-insoluble polymer of the present invention may also contain amine functional monomers selected from the group consisting of tert-butylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylamide, dimethylaminoethyl (meth)acrylate, oxazolidinylethyl (meth)acrylate, vinylbenzylamines, vinylphenylamines, 2-vinylpyridines or 4-vinylpyridines, p-aminostyrenes, substituted diallyl-amines, vinylpiperidines, vinylimidizoles, 2-morpholinoethyl (meth)acrylate, acrylamide, methacrylamide, N-substituted (meth)acrylamides, methacrylamidopropyl trimethyl ammonium chloride (MAPTAC), diallyl dimethyl ammonium chloride (DADMAC), 2-trimethyl ammonium ethyl methacrylic chloride (TMAEMC), quaternary amine salts of substituted (meth)acrylic and (meth)acrylamido monomers, and the like. Suitable levels of monomers having amine functionality for preparing the alkali-insoluble polymer range from about zero (0) to about 15 percent by weight, preferably from about zero (0) to about 10 percent by weight based on the weight of the alkali-insoluble polymer.

The water resistant multi-stage polymers of this invention are useful in applications where water resistance is required. They are more particularly useful as exterior binders for semi-transparent wood stain coatings. The addition of amine functionality, such as for example, dimethylaminoethyl methacrylate (DMAEMA) to the alkali-insoluble polymer to promote association between the alkali-insoluble polymer and the alkali-soluble polymer, provide polymers that are water resistance. It is believed that the association between the amine in the alkali-

insoluble polymer and the acid in the alkali-soluble polymer improves water resistance. However, this is only a theory and is offered only as an explanation of what is believed to happen. The invention is not intended in any way to be limited to such a theory or belief.

The weight ratio of the alkali-insoluble polymer to the alkali-soluble polymer is from about 85:15 to about 15:85, preferably from about 70:30 to about 30:70, and more preferably from about 60:40 to about 40:60.

Multi-stage polymers prepared by the method of this invention may be prepared with or without polyfunctional compounds.

However, chemical association of the alkali-soluble and the alkali-insoluble polymers of this invention may be achieved by polymerizing monomers, in either the soluble or insoluble polymers, in the presence of monomers having polyfunctionality in order to graft the multi-stage polymers of this invention. These polyfunctional monomers are selected from the group consisting of dicyclopentenyl-ethoxy-, dicyclopentenyl-ethoxy-, allyl-, methallyl-, vinyl- and crotyl-esters of acrylic, methacrylic, maleic (mono- and di-esters), fumaric (mono- and di-esters) and itaconic (mono- and di-esters) acids; allyl-, methallyl- and crotyl-vinyl ether and thioether; N- and N,N-di-allyl-, methallyl-, crotyl- and vinyl-amides of acrylic and methacrylic acids; N-allyl-, methallyl- and crotyl-maleimide; vinyl esters of 3-butenic and 4-pentenic acids; diallyl phthalate; triallyl cyanurate; 0-allyl-, methallyl-, crotyl-, 0-alkyl-, aryl-, P-vinyl-, P-allyl-, P-crotyl- and P-methallyl-phosphonates; triallyl-, trimethallyl- and tricrotyl-phosphates; 0-vinyl-, 0,0-diallyl-, dimethallyl- and dicrotyl-phosphates; cycloalkenyl esters of acrylic, methacrylic, maleic (mono- and di-esters), fumaric (mono- and di-esters) and itaconic (mono- and di-esters) acids; vinyl ethers and vinyl thioethers of cycloalkenols and cycloalkene thiols; vinyl esters of cycloalkene carboxylic acids; 1,3-butadiene, isoprene and other conjugated dienes; paramethylstyrene; chloromethylstyrene; allyl-, methallyl-, vinyl- and crotyl-mercaptan; cycloalkenyl-, allyl-, methallyl-, vinyl- and crotyl-mercaptoacetates; bromotrichloromethane; bromoform; carbon tetrachloride; and carbon tetrabromide and the like.

Preferred polyfunctional compounds for use in the present invention are selected from the group consisting of dicyclopentenyl-ethoxy-, allyl-, methallyl-, crotyl- and vinyl-esters of acrylic acid, methacrylic acid, maleic acid (mono- and di-esters), fumaric acid (mono- and di-esters) and itaconic acid (mono- and di-esters); allyl-, methallyl- and crotyl-vinyl ether; N- or N,N-di-, methallyl-, crotyl- and vinyl-amides of acrylic acid and methacrylic acid; N-methallyl and crotyl-maleimide; cycloalkenyl esters of acrylic acid, methacrylic acid, maleic acid (mono- and di-esters), fumaric acid (mono- and di-esters), fumaric acid (mono and di-esters), itaconic acid (mono- and di-esters); 1,3-butadiene; isoprene; paramethylstyrene; chloromethylstyrene; methallyl-, crotyl- and vinyl-mercaptan; cycloalkenyl-, methallyl-, vinyl- and crotyl-mercaptoacetates; cycloalkenyl-, methallyl-, vinyl- and crotyl-mercaptoacetates; dicyclopentenyl-ethoxyethyl esters of acrylic, methacrylic acids and bromotrichloromethane. The polyunsaturated monomers within this list are commonly described as graft-linking monomers which are characterized as having two or more sites of unsaturation of unequal reactivity.

The most preferred polyfunctional compounds for use in the preparation of the alkali-soluble and the alkali-insoluble polymers include those selected from the group consisting of allyl-esters of acrylic and methacrylic acid, cycloalkenyl and crotyl esters of acrylic and methacrylic acid, dicyclopentenyl-ethoxyethyl (meth)acrylate, dicyclopentenyl-ethoxy (meth)acrylate, crotyl mercaptan, cycloalkenyl mercaptoacetates, cycloalkenyl mercaptoacetates, crotyl mercaptoacetate, and bromotrichloromethane. Alkenyl mercaptoalkylates like crotyl mercaptoacetate, allyl mercaptoacetate, and dicyclopentenyl mercaptoacetate have been found to be useful in the preparation of multi-stage compositions described in US-A-4,876,313. US-A-4,876,313 further details and describes other polyfunctional monomers that chemically graft the multi-stage polymer compositions of this invention and is by this reference incorporated herein. Polyfunctional compound(s) may be used at a level of about zero (0) to about 10 percent by weight of the alkali-soluble polymer or the alkali-insoluble, and preferably, from about zero (0) to about 7 percent by weight of the alkali-soluble or alkali-insoluble polymer.

Other additives can be formulated with the multi-stage polymers of the invention to obtain additional benefits. These include the incorporation of metal ions such as Zn, Mg, and Ca into the monomer mixture so as to create metal/carboxylate crosslinks. Monomers crosslinked in this manner enhance water-resistance. Such metal ions can often be conveniently added in a complex form such as, for example, an ammonium complex. In addition, propylene glycol may be used to as a wet edge/open time extender. The amount of such additives is not critical and may be applied in any effective amount.

Additionally, other benefits such as water repellency and water beading in the dried stain film can be enhanced by adding commercial waxes, usually based on paraffin or polyolefin resins. The amount of such additives is not critical and may be applied in any effective amount.

In the paint industry, alkyds or oils are sometimes added to latex based formulations to promote cure and adhesion to difficult substrates. Such modifiers can be used in semi-transparent stains formulated with the multi-stage composition described in the invention. The amount of such additives is, again, not critical and may be

applied in any effective amount

The multi-stage polymers of this invention can be prepared by any of the methods described in US-A-4,876,313 or US-A-4,916,171. There are two preferred methods for preparing the multi-stage polymers of the present invention. Method I is most preferred.

Method I

The first method for preparing the multi-stage polymer of the invention is by sequentially emulsion polymerizing a monomer mixture containing at least one monomer having acid functionality and, optionally, a polyfunctional compound to form the alkali-soluble polymer, followed by a second emulsion polymerization to form the alkali-insoluble polymer in the presence of the previously polymerized alkali-soluble polymer. This method of polymerization is defined as the inverse method.

"Inverse" means that the alkali-soluble stage polymer is prepared first and then the alkali-insoluble polymer stage is polymerized in the presence of the previously prepared alkali-soluble stage. Multi-stage polymers prepared by the method of this invention may be prepared with or without polyfunctional compounds.

The alkali-soluble and alkali-insoluble components are substantially covalently bonded together by carrying out the emulsion polymerization of the alkali-soluble stage in the presence of at least one polyfunctional compound, to graft the alkali-soluble and insoluble polymers. The multi-stage compositions of this invention result in polymer compositions that are stable, water resistant and also exhibit improved lapping when compared to a typical exterior latex polymer.

The multi-stage polymers of Method I are neutralized by dissolving the alkali-soluble polymer with any suitable base or amine. However, the amine or base is preferably selected from the group consisting of ammonia, triethyl amine, monoethanolamine, dimethylaminoethanol, methylaminopropanol, sodium hydroxide and potassium hydroxide. Based on the equivalents of acid in the alkali-soluble polymer, about 0.8 to about 1.5 equivalents of amine or base is added to the polymer compositions to neutralize and substantially dissolve the alkali-soluble polymer so as to form a blend of neutralized alkali-soluble polymer and alkali-insoluble polymer, and an aqueous solution of neutralized alkali-soluble polymer.

Method II

The second method for preparing the multi-stage polymers of the invention includes polymerizing monomers utilizing at least one monomer having acid functionality and, optionally, a polyfunctional compound under emulsion polymerization conditions to form a soluble polymer, neutralizing and solubilizing the soluble polymer with an amine or base as in Method I, then in a separate step, polymerizing a monomer mixture under emulsion polymerization conditions to form an insoluble polymer.

The multi-stage polymers made according to the sequential emulsion polymerization processes of this invention are stable. Stability means that the water-resistant polymers of this invention are useful in environments where water resistance is important. The water-resistant polymers are especially useful where they are used as semi-transparent stains that require water resistance, while maintaining the lapping that is required of a semi-transparent stain. Stability refers to the fact that the films that are made from the polymers produced by the method and composition of this invention have exterior durability and are water-resistant, as measured by wash-off and wet-rub resistance.

The present invention will now be described only by way of example.

In the following Examples the following abbreviations have been used.

ABBREVIATIONS

ALMA	Allyl Methacrylate (crosslinker)
ASR	Alkali Soluble Resin
BA	Butyl Acrylate (monomer)
CTA	Chain Transfer Agent
n-DDM	n-Dodecyl Mercaptan (CTA)
DMAEMA	Dimethylamino Ethyl Methacrylate (amine monomer)
MAA	Methacrylic Acid (acid functional monomer)
MMA	Methyl Methacrylate
MMP	Methyl 3-Mercaptopropionate (CTA)
DCPOMA	Dicyclopentenylloxyethyl Methacrylate
Tg	Glass Transition Temperature (°C)

EXAMPLESPreparation of Soluble and Insoluble Emulsion Polymers/Examples 1-20

A 4-necked round bottom flask, equipped with a condenser, stirrer and thermometer was charged with 1335 grams of DI water, 7.7 grams of Sipon L-22 (28% from Alcolac Inc.) and 2.9 grams of sodium acetate trihydrate. The flask was heated to 85°C under nitrogen. To the flask was added 50 grams of monomer emulsion I (see table below) and a solution of 1.4 grams of ammonium persulfate in 25 grams of DI water. After holding the reaction at 85°C for 15 minutes, the remaining monomer emulsion I containing CTA, if used, and a solution of 1.8 grams of ammonium persulfate in 100 grams DI water was added over 80 minutes. The monomer emulsion container was rinsed with 90 grams of DI water which was added to the flask. Reaction temperature was then held for 30 minutes at 80°C. A solution of 1.4 grams of ammonium persulfate, 2.1 grams of Sipon L-22 and 80 grams of DI water was added to the flask. Monomer emulsion II (see table below) containing CTA, if used, and a solution of 0.72 grams of ammonium persulfate in 100 grams of DI water were added over 80 minutes. Monomer emulsion II container was rinsed with 40 grams of DI water which was then added to the flask. The reaction was held at 85°C for 30 minutes after the additions were completed and then cooled and 103 grams of 29% ammonium hydroxide in 132.8 grams of DI water was added.

Monomer Emulsions

The weight percentage of monomers and chain transfer agents (CTAs) used to prepare the individual monomer emulsions are given in Table 1 (below). The amounts (grams) of water and surfactants are given in the examples below.

Monomer Emulsions for Examples 1-16, 19 and 20 (Example 11 given)		
	Monomer Emulsion I	Monomer Emulsion II
DI water	276	225
Sipon L-22 (28%)	12.9	38.6
Butyl acrylate	244.8	684
Methyl Methacrylate	331.2	36
Methacrylic acid	144	-
Chain Transfer Agent (CTA)		
n-DDM	39.4	-

Monomer Emulsions for Examples 17 and 18 (Example 17)*

	Monomer Emulsion I	Monomer Emulsion II
DI water	225	276
Sipon L-22 (28%)	38.6	12.9
Butyl acrylate	702	432
Methyl Methacrylate		144
Allyl methacrylate	14.4	-
Methacrylic acid	3.6	144
Chain Transfer Agent (CTA)		
MMP		23.8

* Non inverse polymerization is described in US-A- 4,916, 171.

Table 1 Emulsion Polymer Examples 1 to 20

Ex. No.	First Stage			Composition		Second Stage			Composition		Stage Ratio
	BA	MMA	MAA	Other	CTAI	BA	MMA	MAA	CTAI	Other	
1	70	---	30	---	5.47 n-DDM	100	---	---	---	---	50//50
2	52	28	20	---	5.47 n-DDM	95	---	---	---	5 DMAEMA	50//50
3	50	---	50	---	5.47 n-DDM	95	---	---	---	5 DMAEMA	50//50
4	50	---	50	---	5.47 n-DDM	100	---	---	---	---	50//50
5	70	---	30	---	5.47 n-DDM	95	---	---	---	5 DMAEMA	50//50
6	34	46	20	---	5.47 n-DDM	100	---	---	---	---	50//50
7	52	28	20	---	5.47 n-DDM	100	---	---	---	---	50//50
8	34	46	20	---	5.47 n-DDM	95	---	---	---	5 DMAEMA	50//50
9	34	16	50	---	5.47 n-DDM	100	---	---	---	---	50//50
10	34	16	50	---	5.47 n-DDM	95	---	---	---	5 DMAEMA	50//50
11	34	46	20	---	5.47 n-DDM	95	5	---	---	---	50//50
12	34	46	20	---	5.47 n-DDM	95	---	---	---	5 DMAEMA	50//50
13	34	46	20	---	5.47 n-DDM	90	---	---	---	10 DMAEMA	50//50
14	60	20	20	---	3.3 MMP	95	5	---	---	---	50//50
15	60	16	20	4 DCPOMA	3.3 MMP	95	5	---	---	5 DMAEMA	50//50
16	60	20	20	---	5.47 n-DDM	95	---	---	---	---	50//50
17	97.5	---	0.5	2.0 ALMA	---	60	20	20	3.3 MMP	---	50//50
18	94.5	---	0.5	5.0 ALMA	---	34	46	20	3.3 MMP	---	50//50
19	34	46	20	---	5.47 n-DDM	95	---	---	---	5 DMAEMA	50//50
20	34	45.5	20	0.5 ALMA	5.47 n-DDM	95	---	---	---	5 DMAEMA	50//50

1) Weight percent based on stage monomer weight. Solids on solids.
 2) Prepared by Method II. The ammonium hydroxide neutralizer was added to the alkali-soluble polymer before the start of the polymerization of the alkali-insoluble polymer.

Table II - Physical Properties of Emulsions (Ex-
amples 1-20)

Example No.	% Solids	Visc.	pH
1	35.1	82	7.13
2	34.4	46	8.11
3	34.9	178	6.43
4	34.5	200	6.53
5	35.2	858	7.59
6	35.1	244	8.84
7	35.1	388	8.83
8	34.7	142	8.90
9	35.1	147	6.65
10	34.9	534	6.35
11	37.7	1080	8.69
12	36.8	862	8.74
13	36.7	1575	8.75
14	36.4	438	8.66
15	36.6	625	8.52
16	36.6	5200	8.97
17	38.0	650	8.32
18	39.9	825	8.81
19	36.0	198	8.77
20	35.4	431	8.45

The formulation disclosed below was used for Series I, Series II, Series III, Series IV and Series V laboratory screening and exposure evaluations. The formulation was prepared by standard procedures.

Typical Formulation

(Redwood)

5

	<u>kg (Pounds)</u>	<u>l (Gallons)</u>
10 Propylene Glycol (1)	10.5 (23.2)	10 (2.68)
Water	5.3 (11.6)	5.3 (1.39)
Tamol SG-1 (2)	1 (2.2)	0.87 (0.23)
15 Foamaster 111 (3)	0.4 (0.9)	0.4 (0.11)
RO-3097 (4)	7.8 (17.2)	1.6 (0.42)
Minex 7 (5)	27 (59.2)	0.33 (2.73)
20 Example 18 (39.4%) (6)	224 (494.8)	213 (56.31)
Propylene Glycol	25.8 (56.9)	25.2 (6.57)
Aqueous Ammonia (28%)	2.5 (5.5)	2.7 (0.72)
25 Water	109 (240.4)	109 (28.85)
Totals	413.7 (912.0)	378.6 (100.01)

30

PVC = 13.4%

Volume Solids = 23.4%

35

Lbs/Gal = 9.12

(1) Wet edge/open time extender.

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(2) Pigment dispersant

(3) Defoamer

(4) Red Iron Oxide

45

(5) Pigment extender/flatting agent

(6) Emulsion polymer from Examples 1 to 18.

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TEST METHODS AND PROCEDURES

The following methods and procedures were used to obtain the information and test results appearing in Series I, Series II, Series III, Series IV and Series V laboratory screening and exposure evaluations.

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Fog Box Water Resistance

The Fog Box is a test cabinet furnished with water spray nozzles at the top, designed to provide a fine water spray evenly distributed within the cabinet test chamber, simulating steady rainfall. The panel painted

with the test stain is put into the fog box. Test conditions can be varied by varying the air dry time prior to testing, and the length of time the panel is left in the test chamber. During or after exposure in the fog box, the following tests can be made:

- 5 a. **Washoff** - At the end of the preset exposure time, the stained test panel is removed from the box and allowed to dry completely. It is then rated for stain washoff by comparing it visually with an unexposed stained panel. A rating of 10 signifies that essentially no stain was washed off and the soaked board is essentially identical in appearance to the unsoaked control panel. A rating of 0 indicates that all of the applied stain has washed off the panel.
- 10 b. **Wet Rub** - The panel is removed from the box at the completion of the exposure time and immediately tested, while it is still wet, for ruboff by rubbing the stained surface with wet cheese cloth wrapped around the index finger. The rubbing direction is usually across the panel, at right angles to the wood grain, using a smooth linear stroke applying "moderate" pressure with the finger so that the cloth rubs back and forth over the same straight line. Test severity can be varied by varying the air dry time, the soak time, or the number of rubbing strokes. After the panel is dry, it is rated: 10 indicates no stain removal, 0 indicates complete removal of stain down to bare wood.
- 15

Early Water Spot Resistance

- 20 The test panel, smooth cedar with one coat of the test stain, is positioned on a flat level surface and spotted with about 5 drops of water, and left in that position for 5 minutes. At the end of this time, the board is tipped to a vertical position to allow the water to drain off, and then air dried. When dry, the test area is examined for any residual water spotting. No trace of water spot is rated 10; complete washoff of stain down to bare wood is rated 0. The severity of the test can be varied by varying the air dry time before water spotting.

25 Alkali Resistance

- Stained siding beneath windows might be exposed to splash or rundown from ammonia window cleaners. Stained wood framing or siding next to stucco, cement asbestos shingle, or other cementitious building material might be exposed to alkaline rainwater runoff. Because of their alkali-soluble stage component, polymers prepared with the alkali-soluble stage last are vulnerable to attack by alkali. Several tests were designed to evaluate stain binders for alkali resistance.
- 30

- a. **Ammonia Based Household Cleaner** - The test panel, usually a smooth cedar panel cut to measure 12.7 cm x 5.1 cm (5" long X 2" wide), is stained, allowed to dry and immersed in the cleaner for five minutes, after which the test panel is removed, rinsed under running water to remove residual cleaner, and left to dry. No removal of stain is rated 10; completely removal of stain is rated zero (0).
- 35 b. **Alkaline Rainwater Runoff** - The stained test panel is mounted at a 45° angle beneath a separatory funnel equipped with a stop cock. The funnel is filled with pH=11 buffer solution (constant pH, but low ionic strength) and the stop cock adjusted so that the solution drips slowly onto the top of the test panel and runs down across the face of the panel. At the conclusion of the test (500 ml of solution, which takes about an hour to empty onto the panel), the panel is rinsed, dried and rated as above.
- 40

Brushout Lapping

- 45 Stain lapping tests are made on 15 cm x 91 cm (6" x 36") smooth cedar panels, applying the stains with a 5.1 cm (2 inch) nylon brush at a natural spread rate. A 30.4 cm (12-inch) section in the center of the panel is painted with the test stain. After a 10-minute drying interval, the 30.4 cm (12-inch) section at the left end of the board is painted, overlapping the previously stained center section by about 2 inches. After an additional 10-minute drying interval, the 30.4 cm (12-inch) section at the right end of the board is painted, again overlapping the previously stained center section by about 5.1 cm (2 inch). When the panel is completely dry, it is rated for lapping at the two seams. A rating of 10 is perfect, indicating that no lap mark is visible where the two adjacent stained sections are joined. A rating of 0 indicates a very severe mark is visible where the first and second sections overlap. Lapping tests were made at 24°C (75°F), 50% R.H. (Relative Humidity).
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Series I - Test Results for Formulated Stain Properties (10 = Best)				
Formulated Stains based on Example no.	Fog Box Water Resistance			
	Overnight Dry		1 Week Dry	
	Washoff	Wet Rub	Washoff	Wet Rub
11	6	1	3	1
12	9	5	9	4
13	9	7	9	7
18	8	3	8	3

Series I -Test Results

Water resistance in the Fog Box improves with multi-stage polymer prepared using Method I with increasing level of DMAEMA in the alkali-insoluble polymer stage. At 5% and 10% DMAEMA level, water resistance, wet rub resistance, is better in Examples 12 and 13 polymers than in Example 18, where the alkali-insoluble polymer is polymerized as the first stage and the alkali-soluble polymer is polymerized as the second stage polymer as polymerized in US-A-4,916, 171.

Series II - Exposure Data for Stains Given in Series I (above). Overall Appearance Ratings (100 = Best)			
Formulated stain based on example no.	25 Months/south 45°		
	1 coat on cedar	1 coat on plywood	3 coats on plywood
11	73	74	95
12	79	79	91
13	77	74	92
18	68	47	46
17	82	83	89

Series II -Test Results

"Overall Appearance" is a measure of the overall condition of the stained wood surface at the time the readings were taken. A perfect score = 100 indicates no evidence of weathering. Complete deterioration or loss of the stain = 0. These values are averages determined by statistical treatment of the data.

(a) Multi-stage polymers prepared with the alkali-soluble stage first are more durable than the corresponding polymers that are prepared with the alkali-insoluble stage first at comparable hardness (see stains prepared from Example No. 18 versus Examples 11, 12, 13).

(b) Multi-stage polymers prepared with the alkali-soluble stage first have durability equal to softer polymers made with the alkali-insoluble stage first (see stains prepared from Example 17 versus Examples 11, 12 and 13).

Generally, it is recognized that harder polymers are less durable than softer polymers made by the same process. However, as demonstrated in subparagraph (a) and (b) above, this limitation is overcome by the composition, and the method of this invention is used.

Series III - Test Results Obtained With Formulated Stains (10 = Best)				
Stains Prepared with polymers from Example No.	14	15	16	17
Early Water Spot				
1/2 hr dry	9	7	10	2
1 hr dry	10	10	10	5
2 hr dry	10	10	10	8
3 hr dry	10	10	10	8
Resistance to ammonia cleaners and alkaline rainwater runoff				
Ammonia-Containing Window Cleaner 5-min. Immersion				
1 day dry	9	9	5	0
1 week dry	9	9	7	1
Alkaline Rainwater Runoff pH 11				
1 day dry	7	8	4	0

Series III - Test Results

(a) Multi-stage polymers prepared with the alkali-soluble stage first have better early water spot resistance than polymers prepared with the alkali-insoluble stage first and the alkali-soluble stage second.

(b) Stains formulated using multi-stage polymers prepared with the alkali-soluble stage first are more resistant to ammonia cleaners and simulated alkaline rainwater runoff (from adjacent cementitious coatings) than the stains formulated from polymers prepared with the alkali-insoluble stage first and the alkali-soluble stage second.

Series IV - Stain Exposure Data for the Stains Listed in Series II (above)				
	Overall Appearance (100 = Best) 25 Months, South/45°			
Formulated Stains based on polymers from Examples no.	14	15	16	17
Smooth Cedar	86	75	83	79
Rough Cedar	75	72	65	59
T-111 Plywood	83	76	85	77
Plywood (3 cts)	97	93	99	86

Series IV - Test Results

Multi-stage polymers prepared with the alkali-soluble stage first (inverse method) are more durable than the polymers prepared with the alkali-insoluble stage first and the alkali-soluble stage second.

5

Table III									
10	Formulated Stains based on Example No.	Stage I		Stage I/II		Stage II		5-Min.	Wet
		BA	MAA	MMA	Ratio	BA	DMAEMA	W. Spot*	Ruboff*
	9	34	50	16	50/50	100	0	3	5
	4	50	50	0	50/50	100	0	4	3
	1	70	30	0	50/50	100	0	4	6
15	6	34	20	46	50/50	100	0	10	-
	7	52	20	28	50/50	100	0	10	5
	10	34	50	16	50/50	95	5	9	5
	3	50	50	0	50/50	95	5	9	5
	5	70	30	0	50/50	95	5	10	8
	8	34	20	46	50/50	95	5	10	8
20	2	52	20	28	50/50	95	5	10	8
	17	alkali insoluble stage first (control)						7	7
* 10 = Best									

25

Table III - Test Results

(a) Multi-stage polymers prepared with the alkali-soluble stage first that contain 50% MAA in the alkali-soluble stage show the poorest water spot resistance without DMAEMA in the alkali-insoluble stage. These polymers show the greatest improvement in water spot when DMAEMA is incorporated into the alkali-insoluble stage. Wet ruboff resistance also improves with DMAEMA.

(b) Multi-stage polymers prepared with the alkali-soluble stage first with DMAEMA in the alkali-insoluble stage have better water spot resistance than the polymers prepared with the alkali-insoluble stage first and, generally, polymers prepared with the alkali-soluble stage first with DMAEMA in the alkali-insoluble stage have better wet rub resistance than the control (stain prepared with the polymer from Example 17).

<u>Series V - Water Resistance Properties of Semi-Transparent Stains Prepared From Polymers Prepared by Method II</u>				
Formulated Stains Based On Examples No.		Water Resistance (10=Best)		
		1 Hr.	2 Hr.	3 Hr.
45	19	9	10	10
	20	9	10	10
	8	9	10	10
50	17	2	4	6

Series V - Test Results

The formulated semi-transparent stains prepared using the polymers prepared by Method II (Examples 19 and 20) have water resistance equivalent to the polymers prepared by Method I (Example 8); and better water resistance than the polymer where the alkali-insoluble polymer is polymerized as the first stage (Example 17 - non-inverse method of polymerization).

Series VI - Lapping Test Results for Formulated Stains

(10 = Best)

	Formulated Stains based on <u>Example no.</u>	Lapping <u>at 10 min.</u>	Lapping <u>at 20 min.</u>
5			
10	11	9	9
	12	8	7
	13	9	7
15	Latex*	5	3

* Exterior latex polymer - contains no alkali-soluble polymer stage.

20 Series VI - Test Results

Stain brushout lapping obtained with multi-stage polymer prepared using Method I is better than lapping obtained with typical latex polymers made for exterior water-based paints.

25 Claims

1. A water-resistant composition comprising a multi-stage polymer prepared by a sequential emulsion polymerization process comprising an alkali-soluble stage and an alkali-insoluble stage wherein the alkali-soluble stage has an acid functionality greater than the acid functionality of the alkali-insoluble stage and wherein the alkali-insoluble stage is prepared in the presence of the alkali-soluble stage.
2. The composition of Claim 1 wherein the alkali-soluble polymer is neutralized with a base and substantially dissolved to form a blend of neutralized alkali-soluble and alkali-insoluble polymer and an aqueous solution of neutralized alkali-soluble polymer.
3. The composition of any one of the preceding Claims wherein the weight ratio of alkali-insoluble polymer to the alkali-soluble polymer is from about 85:15 to about 15:85.
4. A composition of any one of the preceding Claims wherein the alkali-insoluble stage has amine functionality.
5. A composition according to any one of the preceding claims wherein the alkali-soluble polymer and the alkali-insoluble polymer are chemically grafted together using one or more polyfunctional compounds having two or more sites of unsaturation of unequal reactivity.
6. A method for producing a water-resistant multi-stage polymer prepared by a sequential emulsion polymerization process comprising forming in a first stage a mixture of monomers comprising from about 40 percent to about 90 percent of an alkyl acrylate or methacrylate and from about 10 percent to 60 percent of a carboxylic acid, polymerizing the mixture to form the alkali-soluble polymer, forming in a second stage a mixture of monomers comprising from about 65 percent to about 100 percent of an alkyl acrylate or methacrylate and from about 0 percent to 10 percent of a carboxylic acid, adding the second-stage monomers mixture to the polymerized first stage monomers, and polymerizing the second stage monomers to form an insoluble polymer and wherein the alkali-soluble polymer is neutralized with a base and substantially dissolved to form a blend of neutralized alkali-soluble and alkali-insoluble polymer and an aqueous solution of neutralized alkali-soluble polymer.
7. A method for producing a water-resistant multi-stage polymer comprising forming in a first stage a mixture of monomers comprising from about 40 percent to about 90 percent of an alkyl acrylate or methacrylate



and from about 10 percent to 60 percent of a carboxylic acid, polymerizing the mixture to form the alkali-soluble polymer, neutralizing and solubilizing the alkali-soluble polymer with an amine or base, forming in a second stage a mixture of monomers comprising from about 65 percent to about 100 percent of an alkyl acrylate or methacrylate and from about 0 percent to 10 percent of a carboxylic acid, and polymerizing the second stage monomers to form an alkali-insoluble polymer.

8. A method for producing a water-resistant multi-stage polymer prepared by a sequential emulsion polymerization process comprising forming in a first stage a mixture of monomers comprising from about 40 percent to about 90 percent of an alkyl acrylate or methacrylate and from about 10 percent to 60 percent of a carboxylic acid polymerizing the mixture to form the alkali-soluble polymer, forming in a second stage a mixture of monomers comprising from about 65 percent to about 100 percent of an alkyl acrylate or methacrylate and from about 0 percent to 10 percent of a carboxylic acid and from about 0 percent to 15 percent, preferably from about 0 percent to about 10 percent of a monomer having amine functionality, adding the second-stage monomers mixture to the polymerized first stage monomers, and polymerizing the second stage monomers to form an insoluble polymer and wherein the alkali-soluble polymer is neutralized with a base and substantially dissolved to form a blend of neutralized alkali-soluble and alkali-insoluble polymer and an aqueous solution of neutralized alkali-soluble polymer.
9. A method according to Claim 6 or Claim 7 or Claim 8 wherein the method includes chemically grafting together the alkali-soluble polymer and the alkali-insoluble polymer using one or more polyfunctional compounds having two or more sites of unsaturation of unequal reactivity.
10. A semi-transparent wood stain binder comprising the multi-stage composition having an alkali-soluble polymer stage and an alkali-insoluble polymer stage as defined in any one of Claims 1 - 5 or as prepared according to the method of any one of Claims 6 - 9.